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Surface functionalisation of bacterial cellulose as the route to produce green polylactide nanocomposites with improved properties

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ABSTRACT

The effect of surface functionalisation of bacterial cellulose nanofibrils (BC) and their use as reinforcement for polylactide (PLLA) nanocomposites was investigated. BC was functionalised with various organic acids via an esterification reaction. This rendered the otherwise hydrophilic BC hydrophobic and resulted in better compatibility (interfacial adhesion) between PLLA and BC. A direct wetting method, allowing the determination of the contact angle of polymer droplets on a single BC nanofibre, was developed to quantify the interfacial adhesion between PLLA and functionalised BC. It was found that the contact angle between PLLA droplets and functionalised BC decreased with increasing chain lengths of the organic acids used to hydrophobise BC. A novel method to compound BC with PLLA based on thermally induced phase separation (TIPS) to yield a dry form of pre-extrusion composite was also developed. The mechanical properties of the surface functionalised BC reinforced PLLA nanocomposites showed significant improvements when compared to neat PLLA and BC reinforced PLLA. The thermal degradation and viscoelastic behaviour of the nanocomposites were also improved over neat PLLA.

1. Introduction

Recent interest in greener polymeric materials for general applications such as packaging and the public's growing demand for environmentally friendlier products have sparked the development of green composite materials [1]. One of the most extensively studied renewable reinforcements in this field is cellulose. Cellulose is the most abundant natural polymer, found in plant cells walls, and synthesised by some bacteria and one sea animal (tunicate). The use of cellulosic materials in the production of green composites is well established. Numerous studies have focussed on the use of natural fibres in the production of composite materials [2–7]. More recently, our group [8,9] has successfully deposited BC onto natural fibres, thereby creating hierarchical composites with improved mechanical properties. Extensive research in the field of natural fibre reinforced composite materials is not surprising as natural fibres have many distinct advantages over conventional glass fibres. These include low cost, low density, high toughness, biodegradability and most importantly, carbon neutrality [10,11]. Major automotive companies in Germany such as Mercedes Benz and BMW have started to replace their glass fibre based composites with natural fibre reinforced plastics for their door panel and boot linings [12]. Rieter Automotive won the JEC Composites Award in 2005 for their development in natural fibre reinforced thermoplastic for an under-floor module with integrated aerodynamic, thermal and acoustic functions [13].

Cellulose derived from bacteria such as from the *Acetobacter* species [14] has the advantage of being free from wax, lignin, hemicellulose and pectin, which are present in plant-based cellulosic materials. BC is highly crystalline, with a degree of crystallinity of about 90% [15]. This highly crystalline structure of BC is a property that is favourable for composite production as it results in a high Young's modulus value for BC. It was found that BC possesses a Young's modulus of about 114 GPa and a theoretical Young's modulus of between 130 GPa and 145 GPa depending on the crystallinity [16]. This value exceeds that of synthetic glass fibres (~70 GPa) and aramid fibres (~67 GPa), considering that BC has a lower density (1.25 g cm^{-3}) than glass fibres (2.5 g cm^{-3}). Natural fibres, on the other hand, possess much lower Young's moduli; cotton (12.6 GPa), jute (26.5 GPa), flax (27.6 GPa) and sisal (22 GPa), respectively [17]. Unlike natural fibres, which have to be microfibrillated to produce cellulose strands in the order of 1–100 nm in diameter [18], BC exists naturally as a nanosized material (between 24–86 nm in diameter and several micrometres in length) [14,19] and it has a surface area of about 37 m^2 g^{-1} [20]. Such properties are highly advantageous for the production of composite materials as this implies that for the same amount of material, the interface between the matrix and the reinforcement will be larger for BC compared to micrometre-scale natural fibres. However, these interesting properties of BC do come with a price as BC is extremely hydrophilic in nature. As a result, BC will often have poor interfacial

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adhesion to hydrophobic polymer matrices such as polylactide [9]. However, it can be anticipated that the highly crystalline structure of BC can be retained when the surface of BC is hydrophobised. By preserving the crystalline structure of BC, the Young's modulus will not be affected much and by combining it with a biodegradable polymer, truly green nanocomposites can be produced.

Poly(L-lactic acid) (PLLA) is a biodegradable, hydrophobic aliphatic thermoplastic polyester, derived fully from renewable resources such as corn, starch or sugarcane. It belongs to the family of poly(α-hydroxy acids) and is degraded principally via hydrolysis and to a lesser extent through enzymatic attack [2,21]. PLLA has been used in biomedical applications but its application is somewhat limited by its inherently poor properties such as poor impact strength, low thermal stability and narrow processing window [22]. Modifications to PLLA are necessary so that it can compete with the conventional "big four" (PP, PE, PS, PVC) and other engineering polymers.

In this work we attempt to produce green nanocomposites using functionalised BC to improve the interfacial adhesion between BC and hydrophobic PLLA. BC was functionalised using various organic acids (acetic, hexanoic and dodecanoic acid). A direct wetting method was developed to determine the contact angle of PLLA on the surface functionalised BC. A method based on thermally induced phase separation (TIPS) was adapted from the literature [23] to produce composite microspheres which enables the compounding of dry BC in the polymer using conventional extrusion. The mechanical properties, thermal behaviour and viscoelastic properties of the nanocomposites were also characterised.

2. Experimental

2.1. Materials

PLLA was purchased from Biomer (L9000, MW $\geqslant$150 kg mol^{-1}, D-content $\approx$1.5%) and was used as the matrix for the production of nanocomposites. 1,4-Dioxane (Sigma–Aldrich, ACS Reagent, $\geqslant$99% purity) was used as the solvent for PLLA. Pyridine (analaR NORAMPUR, $\geqslant$99.7% purity), methanol (GPR, $\geqslant$99% purity), ethanol (GPR, $\geqslant$99% purity) and acetic acid (analaR, $\geqslant$99.8% purity) were purchased from VWR. Hexanoic acid (Aldrich, $\geqslant$99.5% purity), dodecanoic acid (Aldrich, $\geqslant$98% purity), dimethyl carbonate (Aldrich Reagent Plus, $\geqslant$99% purity) and *p*-toluenesulfonyl chloride (Aldrich, $\geqslant$99% purity) were purchased from Sigma–Aldrich. Sodium hydroxide (purum grade, pellets) was purchased from Acros Organics. All materials were used as received without further purification. BC was extracted from commercially available *Nata-de-coco* (CHAOKOH coconut gel in syrup, Ampol Food Processing Ltd., Nakorn Pathom, Th).

2.2. Extraction and purification of BC

BC was extracted from *Nata-de-coco* in batches of five jars (of net weight 500 g each). For each batch of five jars, the coconut gels content was rinsed three times with 5 L of de-ionised water and blended for 1 min using a laboratory blender (Waring Blender LB20EG, Christison Particle Technologies, Gateshead, UK). The blended BC was then homogenised at 20,000 rpm in 5 L of water for 2 min using a homogeniser (Polytron PT 10–35 GT, Kinematica, CH) and centrifuged at 14,000g to remove excess water. In order to purify the BC, the centrifuged BC was re-dispersed in 5 L of de-ionised water and heated in 0.1 M NaOH solution at 80 °C for 20 min to remove any remaining microorganisms and soluble polysaccharides [24]. The purified BC was then successively centrifuged and homogenised to neutral pH.

2.3. Surface functionalisation of BC

A functionalisation protocol, developed for the modification of natural fibres was adapted from the literature [25,26] and modified to suit the derivatisation of BC. A dry weight equivalent of 2 g of the purified BC (wet) was solvent exchanged from water through methanol into pyridine at a concentration of 0.3% (g mL^{-1}) to ensure the complete removal of water and methanol. The mixture was homogenised at 20,000 rpm for at least 1 min at each stage to completely disperse BC in the solvent. BC was retained through centrifugation at 14,000g for 15 min prior re-dispersion in the subsequent solvent. The solvent exchange method was used in this case due to the inability of (vacuum) dried BC to re-disperse in any medium because of the strong hydrogen bonds that formed between the nanofibrils. In the final solvent exchange step, the concentration of BC in pyridine was adjusted to 0.5% (g mL^{-1}). From the authors' experiences, this is the concentration at which the mixture can still be stirred properly. At higher concentrations, the mixture becomes too viscous to stir. This BC–pyridine mixture was poured into a 1 L 3-neck round bottom flask and stirred using a magnetic stirrer. 92 g (0.48 mol) of *p*-toluenesulfonyl chloride was added into the reaction vessel and an equimolar amount of organic acids was added into the vessel after the addition of *p*-toluenesulfonyl chloride. The reaction was conducted for 2 h at 50 °C under nitrogen flow to create an inert atmosphere such that water vapour does not affect the esterification reaction. After the reaction, the reaction medium was subsequently quenched with 1.5 L of ethanol and washed three times with 800 mL of ethanol using the previously described homogenisation-centrifugation steps. The product was solvent exchanged from ethanol to water using this method. In order to use the BC in later stages, the product was freeze-dried. Neat and functionalised BC were dispersed in water and dimethyl carbonate respectively at a concentration of 0.4% (g mL^{-1}), flash frozen in Petri-dishes by immersion in liquid nitrogen and subsequently freeze-dried (Edwards Modulyo freeze dryer, UK). The BC functionalised with acetic, hexanoic and dodecanoic acid were termed C_2-BC, C_6-BC and C_{12}-BC, respectively.

2.4. Direct wetting measurement of functionalised BC

In order to investigate the wettability of individual functionalised BC by PLLA melts, a method developed to study the wetting of carbon nanotubes by polymers was adapted from the literature [27]. Approximately 4.4 mg of PLLA was dissolved in 5 mL of chloroform (0.06 wt.%). The solution was left overnight to ensure PLLA fully dissolved in the solvent. Another suspension was prepared by dispersing 3.7 mg of BC in 5 mL of chloroform (0.05 wt.%). This suspension was homogenised for 2 min at 20,000 rpm. The polymer solution was then added into this suspension and the resulting mixture was homogenised again for 2 min at 20,000 rpm followed by ultrasonication for 1 h in a low powered ultrasonic bath to ensure adequate nanofibril dispersion. The mixture of PLLA and BC was added drop wise slowly into a 200 mL hexane/chloroform non-solvent bath (80:20 by weight) under magnetic stirring to precipitate PLLA onto individual cellulose nanofibrils. Precipitates were filtered using a PTFE membrane (0.2 μm pore size, Sartorius Stedium Biotech, UK). The filter cake was heated for 30 min at 180 °C while it is still on the PTFE membrane to melt to polymer. This filter cake was then investigated using a high resolution scanning electron microscope (LEO Gemini 1525 FEG-SEM, Oberkochen, D). The contact angles of the polymer droplets on the cellulose nanofibrils were determined using the generalised height-length method described in literature [28].

2.5. Preparation of composite microspheres with 2 wt.% and 5 wt.% BC loading

Most BC reinforced polymer composites fabrication methods reported in the literature are based on the solution casting method [11,29–31]. Whereby, dry BC sheets are immersed into polymer